Study of simple and low cost solar cell absorber material production process for application in rural areas in developing countries

著者	フーゴ ファスル ラフマン エラワン
number	64
学位授与機関	Tohoku University
学位授与番号	学術（環）第280号
URL	http://hdl.handle.net/10097/00128867

	フーゴ　ファスル　ラフマン　エラワン
氏　　　　　名	Hugo Fathur Rahman Erawan
授　与　学　位	博士（学術）
学 位 記 番 号	学術（環）博第280号
学位授与年月日	令和元年 9 月 25 日
学位授与の根拠法規	学位規則第 4 条第 1 項
研究科，専攻の名称	東北大学大学院環境科学研究科（博士課程）先進社会環境学専攻
学 位 論 文 題 目	Study of simple and low cost solar cell absorber material production process for application in rural areas in developing countries (発展途上国農村部への適用のための簡単で低コストな太陽光セル吸収層の製造方法に関する研究)
指　導　教　員	東北大学教授　高橋英志
論 文 審 査 委 員	主査　東北大学教授　高橋　英志　　東北大学教授　川田　達也 東北大学准教授　上高原　理暢　東北大学助教　横山　俊

論 文 内 容 要 旨

There is one issue that is both an important societal issue and environmental issue that is very important to solve. The lack of electrification in many parts of the world. Many people around the world are still without access to electricity. This means that in their daily life they have subpar access to heating, cooking, lighting, and communication. This can also be a health hazard when they burn fuels for cooking etc. and they breath in the residual gas and particles. The world will and is moving in a direction where electricity will be provided to all of the world's population. The next important question is how will the electricity be produced. From an environmental point of view, there are two possible types of energy that could be provided, greenhouse gas emitting and non-greenhouse-gas emitting. Conventional technologies such as fossil fuel burning power plants fall in the first category and should be avoided if possible. The second category is wide ranging from hydropower, solar cell, wind energy, etc. Most of the non-greenhouse-gas emitting technologies rely on some local resources being available. For example, a large body of water is required for hydropower technology and wind energy needs strong wind patterns. Solar cells is one of the technology that does not heavily relies on the resources and can be used basically everywhere since sunlight is a global resource.

To be able to have solar cells used as the preferred technology in the region currently not being electrified, mostly rural areas in developing countries, we believe that we need a solar cell that has a very low cost. This is because in rural areas and developing countries, the buying power would be much lower than developed countries where the growth of solar cells is currently the fastest. We also believe that not only it should be low cost but it should be produced locally in the developing country. If the country can produced it by itself, this will not only open a new industry that can provide job for the people, it will also incentivize the country to support the growth of solar cell. This is very important as government support is important for growth of solar cells.

In this research we try to develop two new production method of potential low cost solar cells that could be produced in developing countries. The first is the sulfurization of copper indium nanoparticles in aqueous solution. The copper indium nanoparticles were developed by Fujiki et al. from our lab and is produced by reduction of copper and indium ions in aqueous solution. The copper indium particles are then to be converted to copper indium sulfide or copper indium selenide (CIS or CISe) to be used as a solar cell. In our research we explored the potential of converting the alloy particles to CIS in aqueous solution. What we did was mixing the particles in an aqueous solution of sodium sulfide. We examined the sulfurization at various time and temperatures. After sulfurization with 0.5 M of sodium sulfide at various temperature we observe from XRD that at 50°C although the dominant phase is still copper-indium (Cu-In) alloy, a copper sulfide phase is observed. The phase observed is $Cu_{31}S_{16}$. We then did sulfurization at 50°C with 0.5 M sodium sulfide for 3 and 5 hours. The result we observed were that after 3 hours we still had dominant Cu-In alloy peaks with some $Cu_{31}S_{16}$ peaks. After 5 hours, no peaks were clearly observed anymore although some very broad peaks that might belong to $Cu_{31}S_{16}$ were observed. From EDX we observed that the concentration of indium became lower as the sulfurization reaction went on. It was also observed that the solution turn from transparent to faint orange. We believe that what happened was that during the sulfurization the copper and indium in the particles were sulfurized independently forming copper sulfide and indium sulfide instead of CIS. The copper sulfide stayed in the particles, however, the indium sulfide, which we believe were In_2S_3 dissolved in the solution. It is known that In_2S_3 is slightly soluble in sodium sulfide solution. This might also explain the slight change of color in the solution since In_2S_3 has the color orange. Because indium leaks out of the particles, sulfurization of CuIn particles in aqueous solution by sulfurization with sodium sulfide is not possible for the synthesis of CIS nanoparticles.

The second type of solar cell we researched as a potential low cost solar cell to be produced in a developing country is copper zinc tin sulfide solar cell or CZTS. CZTS has some advantages over CIS or CIGS solar cell since it uses only non-toxic and abundant materials, making it even more achievable to be produced in developing countries. Conventionally CZTS solar cells are produced by the deposition of copper, zinc, and tin onto a molybdenum coated glass. The deposited layers are then sulfurized at high temperature by sulfur vapor or H_2S gas. As a result of the sulfurization the copper, zinc, tin, and sulfur are going to react to form CZTS. There is one problem with this method which is the use of molybdenum as the back contact material. Molybdenum needs to be sputtered to be coated on the glass substrate. The sputtering process is a process that requires special and expensive materials which is a potential issue for production in developing countries. Molybdenum has also been known to react with sulfur from CZTS, decomposing the CZTS in a detrimental reaction to the performance of the cell. In this research we adopt a technology that had been researched as a method for production of CIS solar cells but has not yet been studied for CZTS solar cells, the use of copper tape as a substrate and copper source. In the case of the CIS solar cells, indium was electrodeposited on top of a copper tape and subsequently sulfurized to obtain CIS absorber material that was used to make solar cells. The copper tape acts as a structural support and back contact, replacing glass and molybdenum, respectively. The copper tape also acts as the source for copper for the sulfurization reaction so that no copper needs to be deposited. The same concept will be applied to CZTS in this research. Tin and zinc will be deposited on copper tape which will be subsequently sulfurized. As the condition in this method varies greatly from conventional CZTS synthesis method, i.e. the amount of copper will be much larger than tin and zinc, we will start with a study of the phase change during sulfurization to understand the optimal condition for CZTS formation.

First we performed sulfurization at 350, 450, and 550^{o}C for 5, 10, 15, and 20 minutes in a large heater. The sample and the sulfur were both placed in the heater and were in the heater during both the heating and cooling period. We found that with this system even for very short 'sulfurization time' at 550^{o}C the whole copper tape was sulfurized and turned into copper sulfide. This is thought to be because the actual sulfurization time is much longer than the measured sulfurization time which is only measured once the target temperature is reached. Since a temperature of around 550^{o}C or higher will be necessary during sulfurization to obtain CZTS, we decided to change the sulfurization method.

The new method used was optimized to control the sulfurization time. The sulfur was heated separately and the sample was outside the heater during the heating period. Once the heater had reached it target temperature the sample was inserted in the heater and the sulfur gas was let to flow. The sulfurization temperature was at 450, 500, and 550^{o}C with the sulfurization time being 3, 5, and 7 minutes. By using this new sulfurization method, we successfully prevented the complete sulfurization of the copper tape. No CZTS phase was observed but a copper tin sulfide $Cu_2Sn_3S_7$ was obtained in most of the sample. In the samples sulfurized at 550^{o}C for 5 minutes and 7 minutes, the phases observed by XRD were $Cu_2Sn_3S_7$, ZnS, a copper tin alloy, and the copper tape. It is known that CZTS can be formed from the reaction between a copper tin sulfide and zinc sulfide. 30 minutes sintering at 550^{o}C of the sample sulfurized at 550^{o}C for 7 minutes and sulfurization at 600^{o}C for 10 minutes to try to obtained CZTS was done but no CZTS was observed. Instead we found copper sulfide to start forming from the samples. In conclusion we were not able to form CZTS but we did obtain $Cu_2Sn_3S_7$ phase which is also a potential absorber material.

（別紙）

論文審査結果の要旨及びその担当者

論文提出者氏名	Hugo Fathur Rahman Erawan
論 文 題 目	Study of simple and low cost solar cell absorber material production process for application in rural areas in developing countries
論文審査担当者	主査 教 授 高橋 英志 教 授 川田 達也 准教授 上高原 理暢 助 教 横山 俊

論文審査結果の要旨

太陽光エネルギー変換技術は人類の次世代エネルギー獲得技術として欠かせない技術の一つである。最も効率の高い太陽発電はSi系太陽電池であるが、この材料を開発可能な国は、世界中の国の中の10%程度の先進国に限定されており、人口密度も収入も少ない発展途上国では作ることが出来ない。発展途上国で開発できる可能性がある太陽電池として化合物太陽電池が挙げられるが、これを合成する上で最も大きな障害と考えられる個所は、通常はスパッター装置が必要となる、即ち発展途上国では困難な、Mo電極層の形成である。従って、このMo電極層を必要としない構成で光吸収層を形成することが出来れば、化合物太陽電池を簡単簡便に作成可能となると考えられる。この様な観点から、Hugo Fathur Rahman Erawan氏は、発展途上国の農村部でも適用可能な簡単で低コストな方法で太陽光セル用の光吸収層を製造するための技術を開発することを目的とし研究開発を進めた。

第一章は緒論であり、化合物太陽電池材料に関する上述の問題点とそれを解決するための手法について論理的な説明を行った。

第二章においては、本研究室で開発されたCu-In (以下 CI)合金ナノ材料を用いて、常温の水溶液中にて硫化し、Cu-In-S (以下 CIS)光吸収層を合成する為の研究開発を行った。具体的には、金属の錯体構造と溶解度の相関を利用し、常温常圧の水溶液中にてCI合金ナノ材料を硫化させる手法を展開したが、本手法の場合、Cu-SとIn-Sの相分離反応が進行しIn-Sが溶解することを明らかとした。

第三章においては、第二章の結果を踏まえIn-Sの溶解を抑制することを念頭に、液相法と気相法を組み合わせたCu-Zn-Sn-S (以下 CZTS)光吸収層の合成を検討した。特に、上述の通り、発展途上国でも“仕事”として成立させるにはMo電極層の形成を必要としない技術であることが必要となる。そこで、Cuテープ上にZn-Sn層を液相中で形成し、気相中で相変化させることでCZTS合金相の形成を試み、硫化反応系の制御により十分達成可能であることを見出した。

第四章では、第三章の結果を踏まえ、硫化反応過程の詳細な検討を行った。その結果、Zn層の存在が、Sn層の溶融及び凝集を抑制する保護層として作用すること、Mo電極層の代替材料となるCuテープの過度な硫化を抑制し電極層化可能であることを見出した。最終的にCTS光吸収層を簡単簡便に形成可能であることを見出した。

第五章は結論であり、本研究の総括や意義について纏めている。

Hugo Fathur Rahman Erawan氏は第四章に係る内容についてSolar Energyに投稿中である。また、第二章に係る内容については2019年9月に投稿予定である。また、AiMES 2018 (Cancun, 2018年10月)や応用物理学会秋季学術講演会(新潟市、2016年9月)、資源・素材2018(福岡市、2018年9月)などの国内外の会議に参加し、自身の成果について報告を行っている。

以上より、Hugo Fathur Rahman Erawan氏は従来とは異なる視点から太陽電池の実用化を図る手法を考案するとともに、実際にCTS光吸収層を簡単簡便に形成可能な手法を開発することで、彼の考えた論理に対する正当性を検証するなど、先駆的な研究を行った。

よって，本論文は博士(学術)の学位論文として合格と認める。